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Caprolactam Recovery from Aqueous Manufacturing Streams

Union Carbide Corp.
Tarrytown, NY

Prepared for

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Pilot-plant runs using plant samples have demonstrated the feasibility of a novel extraction process for caprolactam recovery from dilute aqueous solutions. Following extraction, aqueous effluent caprolactam concentrations as low as 30 ppm were obtained. Further effluent treatment by activated carbon adsorption reduced the level to less than 2 ppm. In contrast, the commercial multi-effect evaporation process is less economical because much more water is vaporized and the condensate typically contains up to 0.1-0.2 weight percent caprolactam.

Various physical properties were determined. In particular, vapor pressures for the key components were determined using a special high-temperature, low-pressure (vacuum) apparatus designed specifically for this application.

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CAPROLACTAM RECOVERY FROM AQUEOUS MANUFACTURING STREAMS

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

Recovery of process unit wastewater contaminants and reuse of these contaminants in the manufacturing processes is a feasible engineering method to reduce environmental contamination as well as improve the efficiency of manufacturing processes. One method of contaminant recovery from process water streams is extraction of the aqueous waste with specific solvents. This report addresses the potential of solvent extraction methodology for caprolactam aqueous waste streams utilizing laboratory and pilot-scale technology on actual plant samples. Bench and pilot scale data indicate a potential reduction of caprolactam content in wastewater streams from over 1,000 mg/l to as little as 30 mg/l with an energy savings when compared to the existing extraction technology.

William C. Galegar

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Director
Robert S. Kerr Environmental Research Laboratory

ABSTRACT

The project objective is to further develop the Union Carbide Corporation extraction process for caprolactam recovery by testing actual plant samples, conducting pilot plant runs, and obtaining physical property data useful for the process design.

Pilot plant runs have demonstrated the feasibility of a novel extraction process for caprolactam recovery from dilute aqueous solutions. Following extraction, aqueous effluent caprolactam concentrations as low as 30 ppm were obtained. Further effluent treatment by activated carbon adsorption reduced the level to less than 2 ppm. In contrast, the commercial multi-effect evaporation process is less economical because much more water is vaporized and the condensate typically contains up to 0.1-0.2 weight percent caprolactam.

Actual commercial plant samples were used for part of the work and gave similar results to pure component mixtures, indicating that the plant samples tested have no obvious deleterious effects on the process.

Various physical properties, which are needed for this process design, were determined. In particular, vapor pressures for the key components were determined using a special high-temperature, low-pressure (vacuum) apparatus designed specifically for this application.

This report is submitted in fulfillment of Contract No. R-803737 between Union Carbide Corporation and the U. S. Environmental Protection Agency. This report covers the period May 1, 1975 to February 28, 1978; work was completed as of May 3, 1978.

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ABBREVIATIONS AND SYMBOLS

DDP	--dodecylphenol
H.E.T.S.	--height equivalent to a theoretical stage
I.D.	--inner diameter
K_D	--distribution coefficient
L.L.E.	--liquid-liquid equilibrium
µl	--microliter
O.D.	--outer diameter
Temp.	--temperature
V.L.E.	--vapor-liquid equilibrium
x_F	--caprolactam concentration in an aqueous feed
x_{LS}	--caprolactam concentration in a lean solvent
X_F	--feed mass flow rate
X_{LS}	--lean solvent mass flow rate

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We are also deeply indebted to Mr. Roger Kidwell of Monsanto Company, St. Louis, for sharing some of his plant experience with dodecylphenol manufacture which has assisted us in pilot plant operations.

A special gas-chromatographic procedure, devised and operated by Mr. Michael Biller, has been an invaluable tool for samples analysis. His assistance in the bulk of the pilot plant runs and related experiments is also appreciated.

We are also indebted to Mr. Peter C. Dodson for designing and operating the V.L.E. apparatus and assisting in pilot plant runs and related experiments.

SECTION 1

INTRODUCTION

Final product aqueous wash streams having caprolactam concentrations in the range of approximately 1 to 25 weight percent result from the manufacture of caprolactam and from the polymerization of caprolactam to nylon-6. The more concentrated streams are economically recovered by multi-effect evaporation. However, there is no economic incentive to recover the more dilute streams by this energy-intensive method. A properly designed, high-boiling solvent extraction system can be less energy-intensive and extend the lower concentration limit of economically recoverable solutions. Conventional low-boiling solvents, such as benzene, are not economical because large amounts of solvent have to be distilled.

Prior to this project, Union Carbide had developed a laboratory-scale process for caprolactam recovery from aqueous solution. Basically, caprolactam is extracted by DDP (a high-boiling solvent) and recovered from the extract by distillation. The process was further developed during the current project through laboratory testing with plant samples, pilot plant runs simulating the process, and the acquisition of critical physical property data.

SECTION 2

CONCLUSIONS

Pilot plant runs and related experiments have demonstrated the feasibility of the DDP extraction process for recovering caprolactam from the aqueous streams of production plants. This process is more economical than the currently used multi-effect evaporation because less water is distilled (vaporized). Commercialization of this extraction process should extend the lower concentration of economically recoverable aqueous caprolactam solutions from the current 3-5 weight percent limit of the evaporation process down to 0.5 weight percent and very possibly as low as 0.1 weight percent.

The caprolactam concentration in the effluent from Union Carbide Corporation's extraction process is much lower than that of the evaporation process. Evaporator condensates typically can contain as much as 0.1-0.2 weight percent caprolactam, while the extraction process yields an effluent having as little as 30 ppm caprolactam or, if adsorption with activated carbon follows, less than 2 ppm. Carbon treatment of the evaporator condensate may not be practical because the concentration is considerably greater.

SECTION 3

RECOMMENDATIONS

Additional refined V. L. E. data may be required for determining economical stripping column operation. The data accuracy required generally increases with the column (process) size.

More information on size and composition of recoverable aqueous caprolactam streams could perhaps better define further development needs for this process. For example Allied Chemical claims to recycle all its aqueous caprolactam streams and, therefore, does not need a recovery process at its Hopewell caprolactam production plant. The stream sample we received from this plant had only 30 ppm caprolactam. Even if recovery was needed, this is too dilute for economical recovery by extraction or any other means.

SECTION 4

EXPERIMENTAL PROCEDURES

PILOT PLANT PREPARATION

Pilot plant preparation included repairing parts and repiping and adjusting equipment to accommodate this process (Figure 1). Because of a recent flood, all pumps, gauges and electrical equipment near the floor had to be replaced or repaired and cleaned. In addition, seals and joints, loosened by several years of dormancy, were tightened or, in some cases, replaced. The glass distillation column joints needed particular attention because of the high vacuum distillation required. A cracked flange near the bottom leaked excessively during attempts to evacuate the column. The flange was repaired instead of replacing the column because much time would have been required to disassemble the packed column. This repair, which consisted of a wooden plug secured by silicone rubber cement and sealed with vacuum sealing putty, performed satisfactorily for vacuum operation.

Some repiping and valving was done to accommodate the particular flow scheme for this process, including proper connections between the primary and secondary extraction columns and the distillation column. The plate spacing and agitation amplitude in the extraction columns were adjusted for this process to the values in Table 1.

PILOT PLANT DESCRIPTION

After preparation, the pilot plant functioned according to the flow diagram in Figure 2. The initial flow scheme is discussed here, and later modifications will be discussed when appropriate. A typical set of operating temperatures and pressures is included for clarity. Aqueous caprolactam and heptane are continuously pumped from feed vessels into the process lines while DDP is charged batchwise (Stream 10) into the bottom of the distillation column which functions as a holdup vessel.

A centrifugal pump (P-401) circulates the aqueous feed (Stream 1) in the feed drum (D-401) to enhance heating by external band drum heaters. The centrifugal pump also pumps the aqueous feed from the drum to the piston pump (P-402). This pump regulates the feed flow rate into the top of the primary

extractor (C-401). Line heaters (not shown) between the pump and the column automatically control the feed temperature at the column temperature. A separate system controls the column temperature.

A second piston pump (P-405) at the base of the distillation column regulates the solvent flow rate as it cycles between the primary extractor (C-401) and the distillation column (C-403). DDP in the cycle section (Stream 3) from the bottom of the distillation column to the bottom of the extractor is called lean solvent since its caprolactam content is low. Inside the extraction column (C-401), the solvent phase, which is lighter than the aqueous phase, travels upward in droplet form, extracting caprolactam from the downward-flowing continuous aqueous phase. The reciprocating action of perforated plates promotes the mass transfer by forming and maintaining the droplets and minimizing concentration gradients in both phases. Upon reaching the water-extract interface and coalescing at the column top, the DDP is rich in caprolactam and is called the extract. The extract (Stream 4) exits at the column top and proceeds to the distillation column (C-403). A valve (V-403) controls the extract flow rate and maintains a positive extract line pressure. Without it, the distillation column would evacuate the extract line, creating more places for air to leak into the column. This valve is adjusted by visual observation of a pressure gauge. Manually controlled extract line heaters raise the extract temperature to the distillation column feed point temperature. A manually controlled heating jacket surrounds the column base and supplies essentially all the heat for the distillation. Generally kept constant, the jacket control is varied only when the column operating parameters are changed. Insulation and manually controlled heating tape minimize column heat losses which otherwise would be very large for this high temperature distillation.

The packed distillation column fractionates caprolactam and water from the higher boiling DDP. A solenoid-operated reflux splitter controls the fraction of condensate refluxed to the column. The splitter is adjusted manually according to visual observation of the sensitive feedpoint temperature. As the temperature increases above its control point, more of the lower-boiling condensate is refluxed to lower the temperature and vice versa. The column vacuum, provided by a two-stage pump, is maintained to within 1 mm Hg by mercury manometer-controlled solenoids.

The feedpoint is located at the upper section of the column to provide sufficient staging for the difficult caprolactam-DDP separation which occurs below it. Some of the water-DDP separation is achieved here also. Purified DDP exits the column bottom as lean solvent. Performance of this section and, therefore, the lean solvent purity, is sensitive to water concentration at the feedpoint and in the column section above it. A concentration increase, due to an increased extract flow rate or to extract water content fluctuations, results in a higher caprolactam content of the lean solvent. Lean solvent samples are obtained by applying vacuum suction to the lean solvent (Stream 5) coming from the column bottom.

A piston pump regulates the lean solvent flow rate (Stream 3) and pressurizes it from the vacuum pressure (100 mm Hg) of the distillation column to the extractor pressure (our centrifugal pumps do not function at a low suction pressure of 100 mm Hg), returning it to the primary extractor and completing its cycle through the pilot plant. No lean solvent cooling is necessary as line heat losses easily cool it from the high distillation temperature (>250°C) to the extractor temperature (80°C).

The aqueous phase, upon reaching the bottom of the extraction column, is depleted of caprolactam and is called the primary raffinate (Stream 6). It contains a small amount of dissolved and entrained DDP. Quite often, the entrained fraction is the larger one. It consists of extremely small DDP droplets whose upward settling (buoyant) velocities are less than that of the oppositely-moving aqueous phase. Therefore, these droplets are carried downward (entrained) with the aqueous phase. A given degree of column agitation produces a large range of droplet sizes, with the majority large enough to rise against the aqueous flow as required for proper extractor operation. The droplet size distribution broadens with increasing column agitation. In this way, more of the smaller, entrainable droplets are produced, undesirably increasing the total DDP content of the aqueous raffinate. The operating strategy is to agitate as much as possible to enhance mass transfer without excessive entrainment.

The primary raffinate proceeds to the top of the secondary extraction column (C-402) where heptane extracts DDP from it. A small amount of any remaining caprolactam is also extracted. Upon reaching the column bottom, the aqueous phase is depleted of DDP and is called the secondary raffinate (Stream 7). A manually-adjusted valve (V-406) maintains the column pressure and regulates the secondary raffinate flow rate from the column. This stream is the aqueous effluent from this process and may contain as little as 10 ppm caprolactam, 10 ppm DDP, and 100 ppm heptane. Further concentration reduction of these compounds by activated carbon will be discussed in Section 5, Further Treatment of Activated Carbon.

Heptane (Stream 8) is gravity-fed to a piston pump that regulates its flow rate to the bottom of the secondary extraction column. With the heptane phase dispersed, this column operates similarly to the primary extraction column. At the column top, the heptane droplets, high in DDP content, coalesce to form the secondary extract (Stream 9). A manually-operated valve (V-404) maintains the column pressure and regulates the flow rate from the column to a storage drum (D-403), the terminal point for this stream. In an actual process (Figure 1), the secondary extract would be distilled to recover heptane overhead for recycle to the secondary extractor. The DDP bottoms from this distillation would be recycled to the primary extractor. This distillation was not demonstrated in our pilot plant because: a) it is a relatively simple one due to the large boiling point difference between heptane (98°C) and DDP (325°C), and b) substantial pilot plant modification is needed to include this distillation.

ANALYSIS OF CAPROLACTAM AND DDP

A Perkin-Elmer gas chromatograph and an Autolab minigrator were purchased for analyses of the hundreds of samples generated by this project. Allied Chemical provided operating parameters for their caprolactam analysis which aided in the establishment of procedures to analyze dilute aqueous solutions of caprolactam and DDP and dilute solutions of caprolactam in DDP. Operating parameters are shown in Table 2. Flame ionization detection and an internal standard, acetophenone, provide the sensitivity and accuracy needed in the ppm concentration range.

SECTION 5

RESULTS AND DISCUSSION

INITIAL EVALUATION

Before pilot plant work was begun, an aqueous plant sample, dilute in caprolactam, gave extraction and distillation results in good agreement with pure component data. This evaluation was performed to determine whether other impurities (if any) in the plant stream significantly affected the extraction or distillation parts of this process. The sample was obtained from a process column overhead of an Allied Chemical Company plant, a major U. S. caprolactam producer. Our analysis showed this sample to contain 30 ppm caprolactam. To avoid the analytical error at this low concentration, additional caprolactam was added to increase the concentration to 600 ppm.

The extraction was performed at 80°C in the apparatus shown in Figure 3 wherein equal parts by weight of the aqueous solution and DDP were contacted and allowed to reach equilibrium. Analysis of raffinate and extract phases by gas chromatography showed that 95 percent of the caprolactam was extracted from the aqueous phase. For this project, the primary extract and raffinate phases are the DDP (solvent) and aqueous phases, respectively, at equilibrium with respect to the caprolactam content. The distribution coefficient

$$K_D = \frac{\text{weight percent caprolactam in the extract}}{\text{weight percent caprolactam in the raffinate}}$$

for this extraction was calculated to be about 20. This value is in good agreement with our laboratory data previously obtained using pure water, caprolactam, and DDP (Figure 4). Therefore, it was concluded that impurities present in the plant samples tested have no significant effect on the extraction part of this process.

The extraction distillation was performed in a 2"-I.D. Oldershaw column at 45 mm Hg pressure. Operating parameters are given in Table 2. The caprolactam content of the extract was reduced to 592 ppm. This is in good agreement with laboratory distillation data using pure water, caprolactam, and DDP, as shown in Table 3. With the plant sample evaluation completed and satisfactory, the pilot plant phase was begun.

PILOT PLANT RUNS

Solvent Stripping

Several batches of commercial DDP were stripped of light ends in the distillation column to remove lower-boiling alkylphenols which form maximum boiling azeotropes with caprolactam. If not removed, they would reduce the efficiency of the caprolactam-DDP distillation during the pilot plant runs. Each batch was stripped at 40 mm Hg and 250°C for about 8-10 hours.

During these distillations, useful column operating experience was obtained. Excepting the vacuum system, the column is controlled manually, which requires some familiarity. At the low pressure of 40 mm Hg, we found that the column can easily be flooded by high vapor rates and we employed a maximum jacket heat input to prevent flooding. A preliminary heat balance revealed a large heat loss through the insulated column wall. To help to compensate for this, the column heaters were adjusted to near-maximum output.

The bottoms product from each distillation was saved for use as a solvent. Gas chromatograms showed reduced light ends peaks of the bottoms products similar to those of laboratory-stripped DDP, indicating that the pilot plant-stripped DDP was suitable for use.

First Process Run Series

During this 168-hour run series, caprolactam recovery was good but less than expected. A summary of problems and suspected causes is shown in Table 4. The distillation column was started up first, as it required several hours to reach equilibrium. Then the primary and secondary extraction columns were started, putting the process into full operation. The operating parameters and stream conditions for this run series are summarized in Table 5, Columns (Runs) 1A-1D. For each parameter set, the pilot plant was allowed to equilibrate for at least 1 hour before samples were taken. This allowed each component (e.g., distillation column) to equilibrate individually, but not with the whole pilot plant. This would have required several hours and is neither practical nor necessary for meaningful results.

For Runs 1A-1D, the caprolactam-supplemented 600-ppm plant sample from Allied was used. The best caprolactam recovery is about 89 percent (Run 1C). Using literature methods (1), the height equivalent to a theoretical stage (H.E.T.S.: a measure of extractor efficiency) is calculated to be about 35 inches. Literature data (2) for the Karr column show the H.E.T.S. is usually below 15 inches. The initially suspected cause of this low extractor efficiency was the lean solvent which contained about 1500 ppm caprolactam -- about three times that of the laboratory distillation bottoms. A high lean solvent caprolactam concentration may reduce caprolactam recovery by limiting the theoretical

equilibrium recovery attainable.

$$\text{Theoretical Equilibrium Recovery} = \frac{x_F - (x_{LS}/K_D)}{x_F} \times 100\%$$

$$\text{When } \frac{X_F}{X_{LS}} < K_D$$

Where x_{LS} = concentration of caprolactam in the lean solvent

x_F = concentration of caprolactam in the feed

X_{LS} = lean solvent mass flow rate

X_F = feed mass flow rate

Initially suspected causes of the poor lean solvent purity were insufficient solvent stripping of light ends and insufficient column staging. Attempting to correct for the latter, column pressure and temperature were increased in Runs 1C and 1D. Laboratory distillation experience prior to this project suggests the relative volatility (ease of separation by distillation) between caprolactam and DDP increases with increasing temperature. Doing so produced a small but insufficient improvement in lean solvent purity.

Additional Solvent Stripping

To determine whether insufficient light ends removal had caused the poor lean solvent purities (the mechanisms for which were discussed in Solvent Stripping) in Run 1, the solvent was restripped semicontinuously. This differed from the simpler batch stripping in that the bottoms product was drawn off during the distillation rather than after the distillation had been shut down, which allowed the column liquid, possibly containing some light ends, to drain into the bottoms product.

After all the bottoms were removed, the column was shut down and cleaned with isopropanol to wash away any remaining light ends. The restripped solvent was charged to the column bottom for a second process run.

Second Process Run Series

In spite of additional solvent stripping and other parameter changes, results from this series of runs are very similar to the first. For Runs 2A and 2B, the feed caprolactam concentration is the same as in Run Series 1. The lean

solvent purity and caprolactam recovery are the same as or less than in Run Series 1, which indicates that the additional solvent stripping has little effect. In contrast to Run Series 1 results, a higher distillation column pressure (83.5 mm Hg versus 38.5 mm Hg) did not improve the lean solvent purity in 2B over that of 2A, which indicates that another parameter has a greater effect on the recovery.

To further investigate the caprolactam recovery problem, we switched to a feed containing about 1 percent caprolactam prepared from pure water and caprolactam. If lean solvent purity had been limiting the recovery, then this higher concentration should improve the recovery. For Run 2F, the recovery is 93 percent -- somewhat better, but still not as good as expected. For this run, the column agitation is lower than for the previous runs because, at the higher caprolactam concentration, the water-caprolactam-DDP system is more prone to entrainment. This is evidenced by the high DDP content of the primary raffinate in 2D and 2E where greater agitation was used. This condition is not practical and is not recommended for proper process operation.

Changing the primary extractor dispersed phase had little effect on caprolactam recovery. The high viscosity of the solvent (27 c.p. - Figure 5) was suspected to cause low mass transfer and low recoveries. To provide more agitation to overcome this effect, the solvent was made the continuous phase. However, Run 2G shows essentially no improvement over 2F; as will be shown later, this method is simply not sufficient to overcome the viscosity effect.

Third Process Run Series

Raising the column temperature is found to be an unsatisfactory method of reducing the solvent viscosity. It had been planned to operate the column at 127°C where the solvent viscosity is about 5 c.p. (Figure 5), a viscosity at which satisfactory literature data had been obtained with other systems (2). Upon beginning this run, the column heaters were soon discovered to be inadequate to achieve this temperature; therefore, we obtained Run 3A at 92°C and then stopped this run series. Essentially no recovery improvement was noted with this incremental temperature change. The column heating capability was not improved because subsequent laboratory solubility experiments showed that the water solubility in DDP was too high at 127°C (Figure 6). Higher water concentrations of the extract increase the load on the distillation column.

Fourth Process Run Series

Extraction Runs--

The primary extractor efficiency increases significantly when the solvent viscosity is reduced by adding heptane. Laboratory viscosity measurements of DDP-heptane mixtures show that the addition of 10-30 weight percent heptane markedly reduces the viscosity of DDP (Figure 7). A 30 percent heptane/70

percent DDP mixture was employed as the solvent for Runs 4A-4F. The distillation column was not operated for these runs because there was no available method for providing good and constant ratio mixing of the lean solvent with heptane. Instead, a batch of this mixture was prepared before the run and fed from a drum to the solvent flow controlling piston pump. The primary extract was simply fed to the dormant distillation column where it was stored for a subsequent batch distillation. The heptane-DDP flow rate was adjusted to be equivalent to 32 ml DDP/min, the flow rate used in 2D-2G. Except for this adjustment, the operating parameters of 4A, 4B and 4C are identical to those of 2D and 2E. The caprolactam recovery is much higher, presumably due to heptane's viscosity-reducing effect. At the lower temperature of 60°C, Runs 4D-4F gave similar caprolactam recoveries but resulted in much less DDP in the primary raffinate. This is because the higher interfacial tension between the solvent and aqueous phases at the lower temperature decreases the solvent phase breakup into the very small, entrainable drops.

Extract Batch Distillation--

This distillation yielded a much better lean solvent purity than did the previous continuous ones. The improvement is attributed to the additional column staging made available by the batch method and to the separate removal of water (and any other low-boiling compounds present) which hinders the more difficult caprolactam-DDP separation. This distillation, being batch, necessarily had to be run following the extraction run. The objective was to demonstrate whether distilling water (and heptane) first, and then caprolactam, would result in a better lean solvent purity. This separation could also be performed continuously using two columns, however the extra column was not available in our pilot plant. The extract from Runs 4A-4F was, therefore, batch-distilled under the usual operating conditions as shown in 4G-4M. Heptane and water were the first components to come overhead. Initially, the pressure was maintained at 100 mm Hg. to assure adequate condensation of the 30°C aqueous overhead. As the distillation progressed and the head temperature increased because of the buildup of higher-boiling light ends, the column pressure was reduced to 75 mm Hg. After most of the water and caprolactam was removed, an intermediate fraction was removed which consisted of caprolactam, water, heptane, and light ends. The light ends source would be the plant feed and/or oxidative decomposition products from the distillation column (solvent decomposition will be discussed later).

In Run 4L, a pure caprolactam fraction was obtained as evidenced by the constant head temperature of 187°C. Finally, the head temperature began rising, indicating that most of the caprolactam was removed and the higher boiling DDP solvent was beginning to come overhead. The distillation was continued until the temperature rose to 235°C (Run 4M), significantly above the caprolactam overhead temperature, assuring a good caprolactam removal from the column bottoms. The bottoms analysis (4M) showed 466 ppm caprolactam, a large

reduction below the 1000-3000 ppm range typical of the previous runs and agreeing well with the laboratory value of 592 ppm.

Fifth Process Run Series

For this final process run, caprolactam recoveries were the highest of all runs. However, a dispersal phase change for the secondary extractor failed to improve its efficiency as expected. For these runs, the primary extractor was operated as in Runs 4D-4F, the only difference being the lower lean solvent caprolactam concentration. The greater caprolactam recoveries are attributed to this. Although the total extracted amount is not much greater, the primary raffinate concentration is about half that of Runs 4D-4F.

The secondary extractor dispersed phase was changed to aqueous in an attempt to improve the efficiency. Earlier Runs 1C-1D gave good DDP recovery when the heptane flow rate was at the "higher", but still very economical, rate of 9 ml/min, leaving as little as 9 ppm DDP in the secondary raffinate. However, cutting the heptane rate to 7 ml/min greatly reduced the DDP recovery as seen in the remaining runs. Extraction data obtained several years ago, and our extraction experience, suggest that distribution coefficients for DDP between heptane and water should be greater than 1000/1 in favor of the heptane. Therefore, it was reasoned that the 1/18 heptane-to-water ratio (at 9 ml heptane/min) is more than sufficient to extract DDP.

The secondary extraction column was suspected of being too large, thus resulting in an insufficient interfacial area. Karr column literature data (2) show a maximum combined phase flow rate of about 1000 gph/ft^2. In contrast, the secondary extractor combined rate is 123 gph/ft^2. Of this, the individual heptane rate is only 6.5 gph/ft^2. Visually, the dispersed heptane droplets are very sparse. In addition, the large density difference between heptane and water causes the droplets to travel quite quickly up the column. Two methods of slowing the droplet ascent are by producing smaller, slower-ascending drops and by increasing the continuous phase velocity. Smaller droplets could not be formed because extreme agitation is required to overcome the heptane/water interfacial tension (36.2 dynes/cm at 20°C). A smaller diameter column, which is not available in our pilot plant, will increase the continuous phase velocity and thereby reduce the droplet velocity to the column. In this way, droplet residence time and column efficiency can be increased.

Instead, an efficiency improvement was attempted by changing the dispersed phase. Having a flow rate 18 times larger than the heptane phase, the aqueous phase, when dispersed, should provide much more interfacial tension area and increase the column efficiency. However, as seen in Runs 5A-5D, essentially no DDP was extracted. This was partially due to the preferential wetting of the glass column walls by the aqueous drops. During the runs, the bulk of the aqueous phase was seen cascading down the column wall in spite of

maximum agitation. The droplets which were produced were large and, therefore, resulted in small interfacial area (mass transfer area).

A secondary cause of the poor recovery was that water viscosity is about 5 times that of heptane. This reduces the mass transfer in the dispersed phase.

Modified Process Flow Diagram

The above results suggest an improved process flow scheme shown in Figure 8. Schematically, the primary and secondary extractors in Figure 1 are combined, and an additional distillation column has been added. This process incorporates heptane addition to DDP for increased extractor efficiency and distilling water separately from caprolactam which improves the distillation column efficiency.

The flow scheme is similar to the original process. The aqueous caprolactam feed enters at the extractor top and flows downward. DDP enters at the extractor midsection as lean solvent and flows upward, extracting caprolactam from the aqueous phase. Heptane enters at the extractor bottom and flows upward, extracting DDP from the aqueous phase. The heptane-DDP extract combines with the lean solvent at the extractor midsection and, in so doing, reduces the solvent viscosity. The extract exits at the extractor top and contains DDP, heptane, caprolactam, and some water. Heptane and water are distilled from this extract in the drying column. Being very immiscible with one another, heptane and water in the overhead are separated by decanting. Part of the heptane is refluxed to the drying column; the remainder is recycled to the extractor column. The water from the decanter is combined with the extractor raffinate, forming the process effluent.

DDP and caprolactam constitute the drying column bottoms product which is fractionated into caprolactam (overhead) and DDP (bottom) in the stripping column.

Further Treatment by Activated Carbon

Batch and continuous column tests show that activated carbon adsorption is a good method for removing the trace amounts of caprolactam, DDP and heptane in the secondary extractor raffinate. This polishing step can be used when very low effluent concentrations are desired.

As discussed previously, pilot plant runs have produced an aqueous stream containing as little as 30 ppm caprolactam, 10 ppm DDP, and 20 ppm heptane. These levels are very low for a recovery process. Although it should be possible to reduce the DDP concentration by increasing the secondary extractor length, it offers little overall improvement since the caprolactam and heptane concentrations are not reduced by this parameter change. The lean solvent purity (caprolactam content) lower limit appears to be about 500 ppm. This, in turn, places a lower

limit on the caprolactam concentration in the primary extractor raffinate. The lower limit of heptane in the secondary raffinate is simply the solubility of heptane in water.

To learn how effective carbon adsorption is in further reducing the above concentrations, batch adsorption experiments were conducted on dilute aqueous solutions of caprolactam and DDP. Heptane was not included here, as hydrocarbon adsorption by activated carbon is well known. The results are shown in Table 6. The distribution coefficient measures how well caprolactam and DDP are adsorbed. It is the ratio of the weight percent material adsorbed on the carbon divided by the weight percent material in the aqueous solution at equilibrium. The former is calculated by dividing the total material recovered from the aqueous solution by the sum of the total weight of carbon employed in the experiment and the removed material weight. For most of the experiments, the solution concentrations are below (probably significantly below) the detection limits as indicated. Although this does not allow the calculation of exact distribution coefficients, it does show that the amount of carbon needed to treat the secondary raffinate is very small. A continuous column test (results shown in Table 7) shows similar results. Here the starting solution is the secondary raffinate from pilot plant Run 5C.

Solvent Decomposition

Oxidative decomposition darkened the solvent but did not reduce its extraction capacity. The glass distillation column had numerous joints and, although all were tightened, air leakage into the column, combined with the high distillation temperature, was a suspected cause of solvent discoloration.

Decomposition experiments verified the decomposition to be oxidative and not simply thermal. To determine this, the air leakage into the distillation column was measured and the total amount calculated for 168 hours' (1 week's) operation. This amount was divided by the total amount of solvent in the pilot plant system. A mixture of the above ratio was prepared using pure DDP and heated to 250°C for 168 hours. A second sample of DDP and nitrogen was heated identically. The results are impressive (Table 8). The air-containing sample turned dark brown and was very similar in appearance and color to the darkened pilot plant solvent. The second sample, containing no oxygen, was essentially unchanged in color.

These results clearly indicate that DDP decomposition is caused by the presence of oxygen at elevated temperatures. Interestingly, the air leakage rate for our distillation column falls within the limits for typical "commercially tight" units. However, it is possible to design a commercial unit to be practically airtight. DDP is commercially purified by a distillation in such a column (according to personal communication with Mr. Roger Kidwell, Monsanto).

A laboratory extraction using pilot plant lean solvent having about 300 hours' operating time showed results similar to those obtained with pure DDP (Figure 4). Although these results do not guarantee that solvent oxidation, if allowed to occur at rates experienced in our pilot plant over a longer period of time, will not reduce the solvent extraction capacity, the results do indicate that any effects are very gradual.

Physical Property Data

Other physical properties needed for process design that were measured are DDP density, DDP solubility in water, and interfacial tensions for the water-caprolactam-DDP system. The results are shown graphically in Figures 9, 10 and 11, respectively. The experimental methods employed are given in the Appendix.

In addition, consistent, but very abnormal, pressure data were obtained for the caprolactam-DDP mixtures. Pure component and binary vapor pressure data are needed for the design of distillation columns. For this process containing water, caprolactam, DDP and heptane, there are four pure components and six binary pairs. However, it is not necessary to obtain data for which sufficiently accurate data are available in the literature or for pairs that have large boiling point differences for which calculated ideal vapor pressure data are sufficient. Heptane, water, caprolactam, and the caprolactam-water pair and heptane-water pair fall into the first category. The heptane-caprolactam, heptane-DDP, and water-DDP pairs fall into the second category. No literature data are available for DDP or the caprolactam-DDP pair. These and caprolactam vapor pressure data are the key components needed for the design of the system. Therefore, these vapor pressure data were obtained, including those for caprolactam, since precision can be lost when key vapor pressure data are obtained from different sources.

A special apparatus was built for this purpose (Figure 12). The key apparatus components are listed in Table 9. It was designed to operate up to 340°C and at pressures from 10^{-4} psia up to 100 psia. A differential pressure transducer measures the pressure difference between the sample and a reference pressure. For our experiments, the reference is a vacuum source that was low enough to be considered 0 psia. Therefore, the transducer gave direct sample pressure headings. The data for this project were taken at high temperatures and low pressures, requiring that the apparatus used have several features. To minimize air leakage into the system, most connections were welded. Special vacuum fittings were used for the few connections which had to be separable. To provide a uniform temperature, the apparatus was enclosed by an oven. The differential pressure transducer sensor also had to be in the oven to maintain it at the system pressure so that the sample vapors do not condense in the transducer sensor. This condensation is undesirable because a) it allows fractionation of

the sample which changes its composition and b) liquid(s) in the sensor, especially polar ones, cause inaccurate, nonreproducible readings because they interfere with the capacitor-type sensor. After operating the apparatus, we discovered that, for the more polar caprolactam, maintaining the sensor at the system temperature was not sufficient to prevent this sensor malfunction. Heating tape, wrapped around the sensor, maintains the sensor temperature 40°C above the system temperature, eliminating the problem.

During operation, once the system temperature is reached, the sensor requires two hours to thermally equilibrate because the sensor generates some heat and is temperature-sensitive. The system has to be evacuated for at least 30-60 minutes to remove all the air and, during operation, shorter evacuations have to be performed about every 2 hours to remove air that has leaked into the system. The evacuation time is kept approximately inversely proportional to the system temperature to minimize sample loss. Generally, the evacuations are done as long as possible without noticeable sample buildup (sample loss) in the dry ice trap (not shown) located along the vacuum line between the oven and the vacuum pump (not shown).

The pure component data for caprolactam and DDP are shown in Figures 13 and 14, respectively. The caprolactam data agree reasonably well with literature data (8). The vapor pressure data for caprolactam-DDP mixtures shown in Figure 15 are very consistent with one another. However, when compared to the pure component data, the mixture data are unexpectedly high in the low temperature range (100-175°C) and somewhat low in the high temperature range (230-250°C). This does not necessarily mean that the data are invalid or that they are accurate enough for distillation column design, however, as process scale increases, so does the data accuracy required for economic process design.

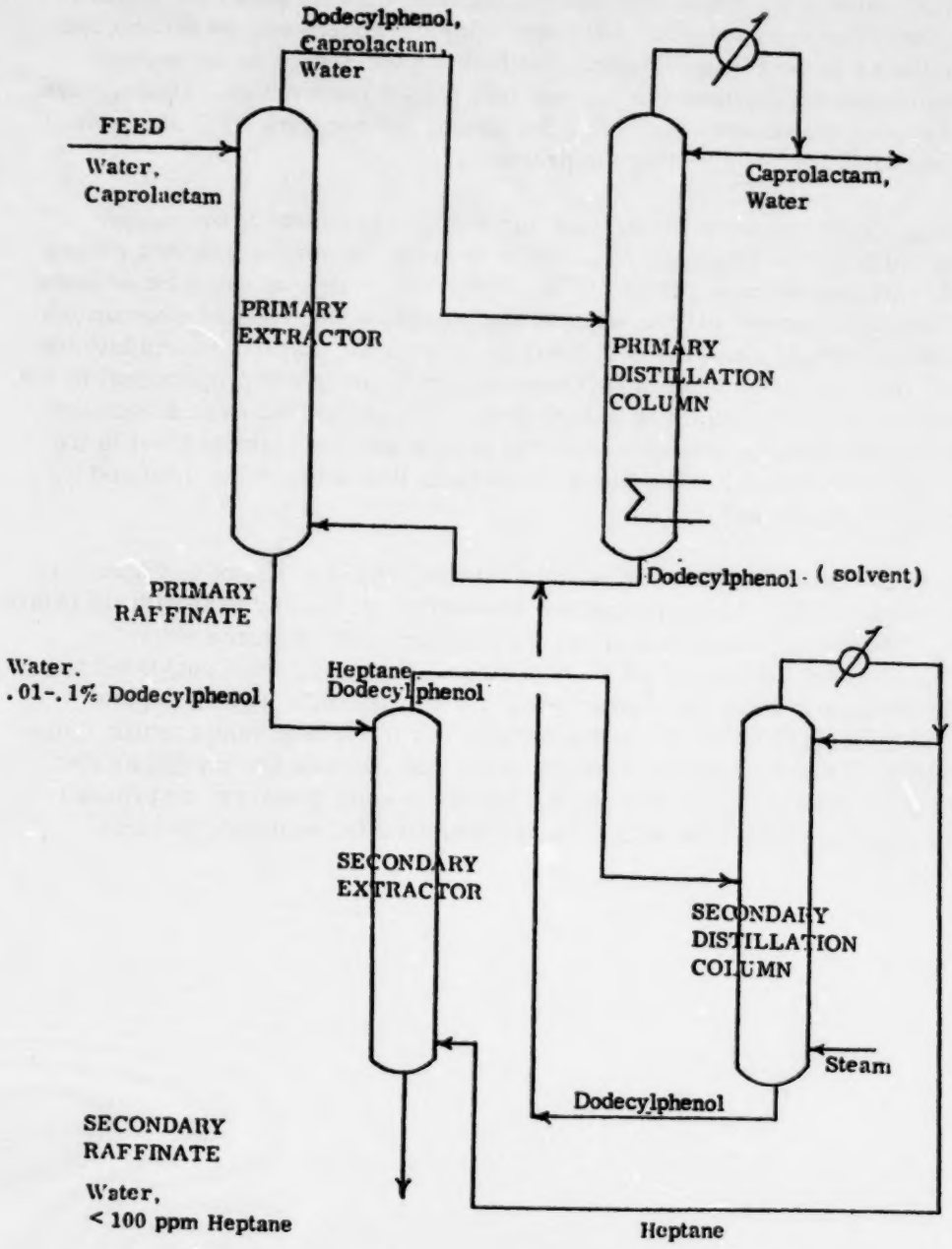

Figure 1. Basic Union Carbide Corporation process for caprolactam recovery from aqueous solution.

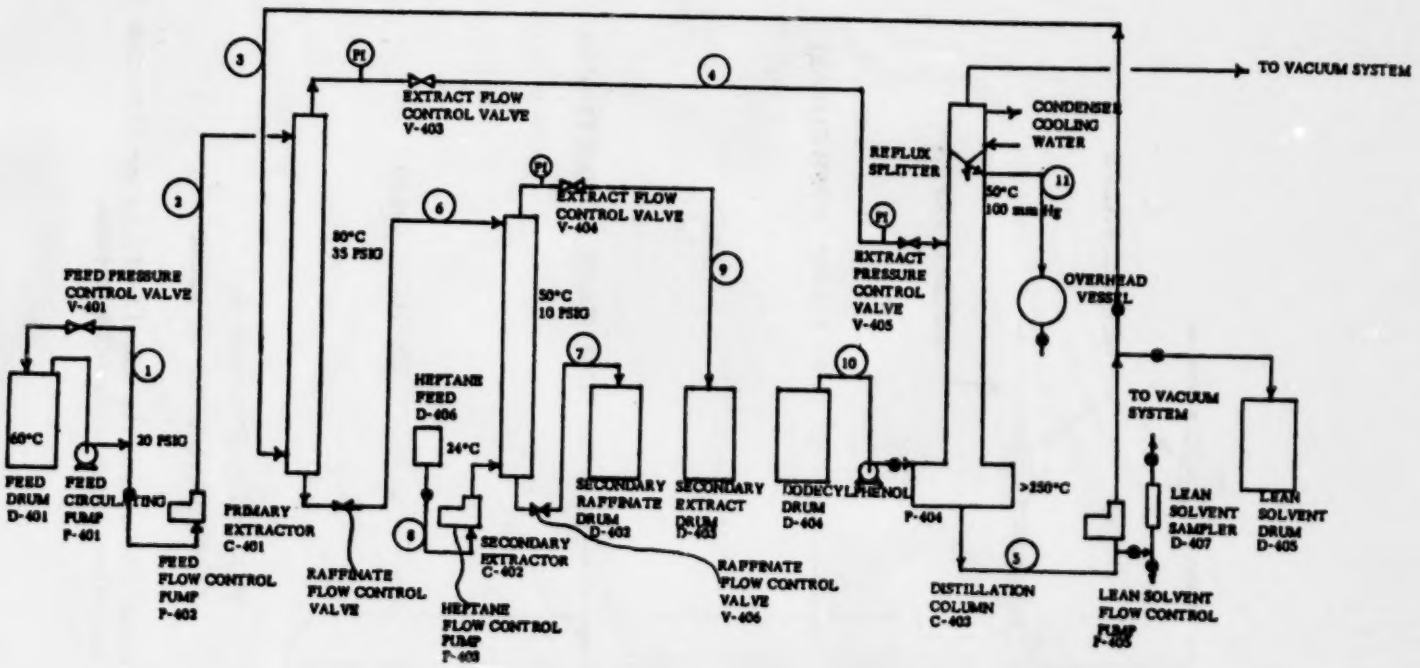

Figure 2. Pilot plant diagram for the Union Carbide Corporation caprolactam extraction process.

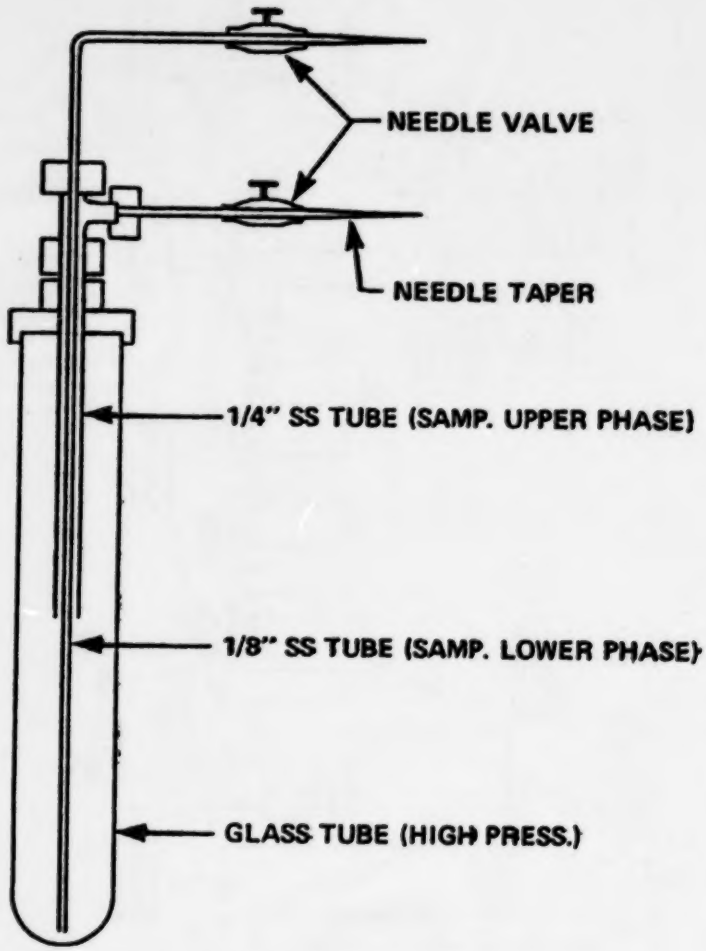
NEEDLE VALVE
NEEDLE TAPER
1/4" SS TUBE (SAMP. UPPER PHASE)
1/8" SS TUBE (SAMP. LOWER PHASE)
GLASS TUBE (HIGH PRESS.)
PRESSURE UP TO 500 psi
TEMPERATURE UP TO 200°C

Figure 3. Apparatus for obtaining liquid-liquid equilibrium data for the water-caprolactam-DDP system.

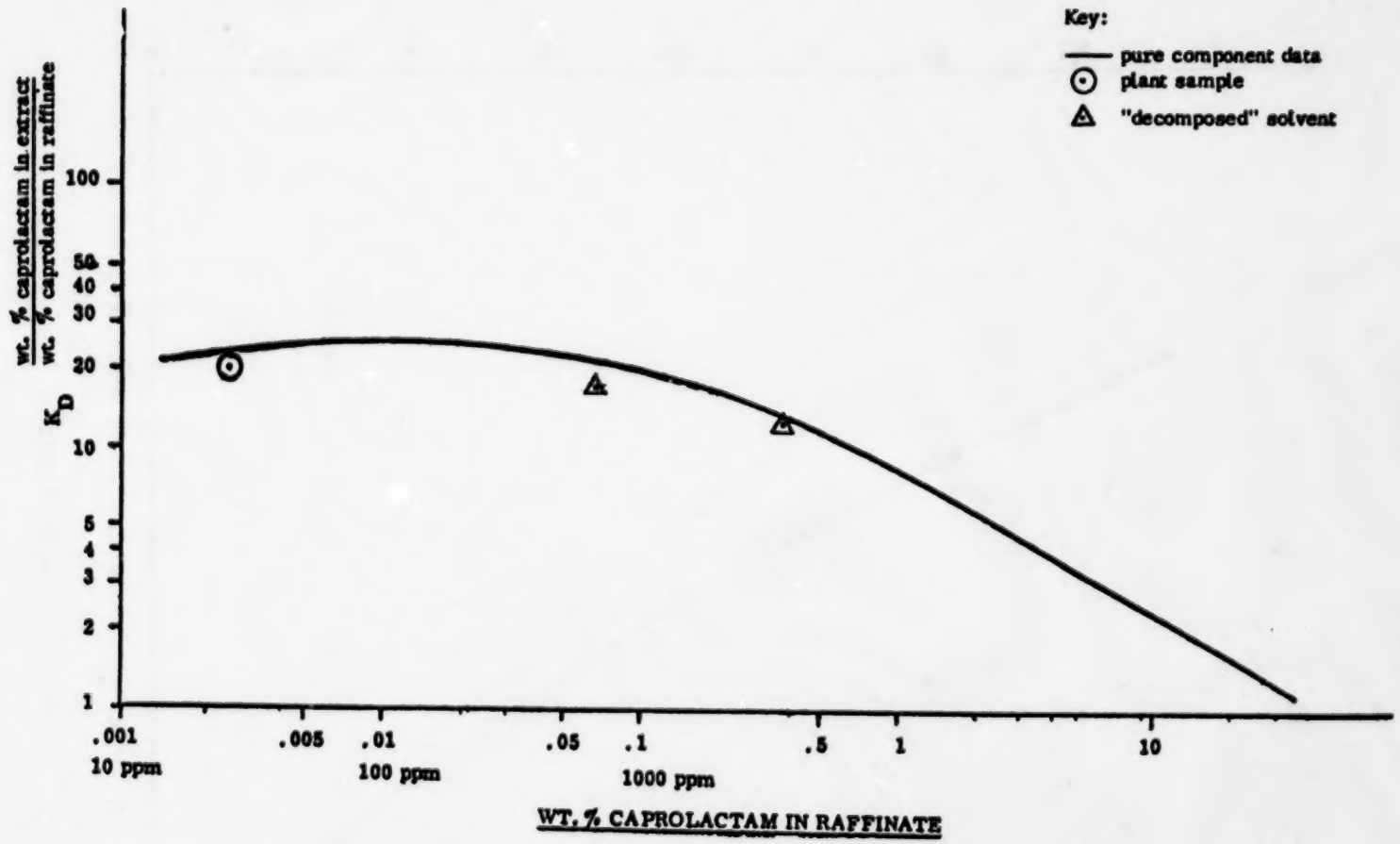

Figure 4. Distribution coefficient (K_D) for caprolactam between DDP and water at 80° C.

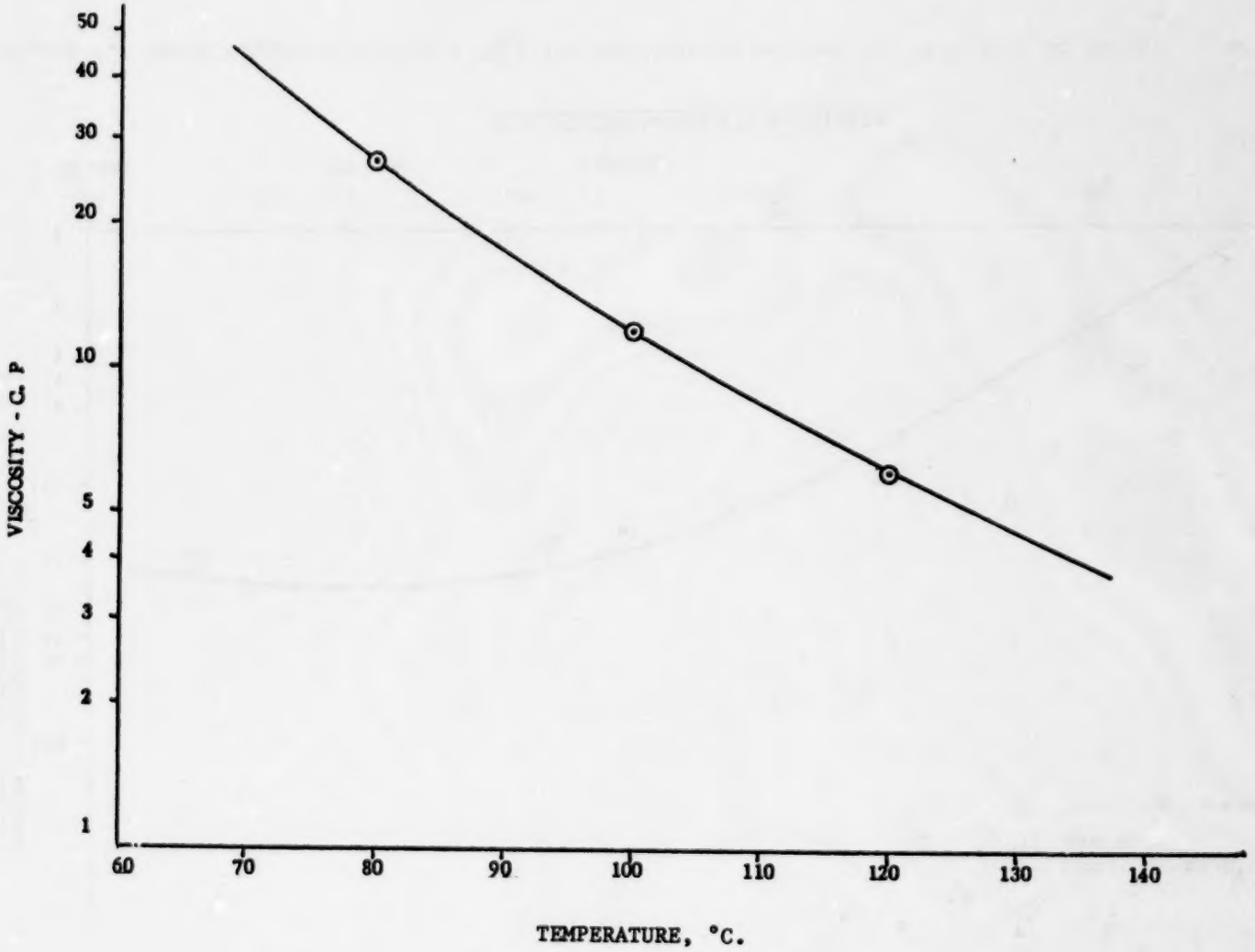

Figure 5. DDP viscosity versus temperature.

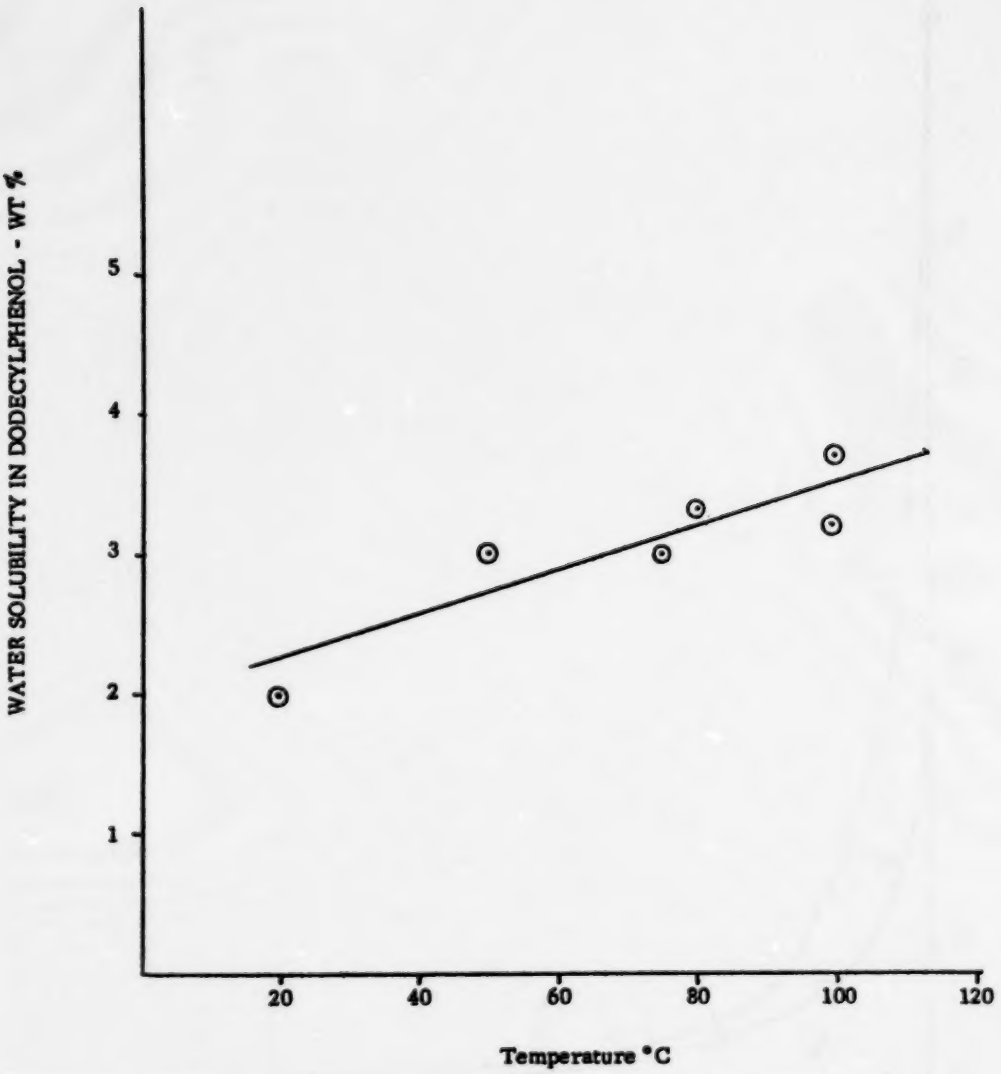

Figure 6. Solubility of water in DDP versus temperature.

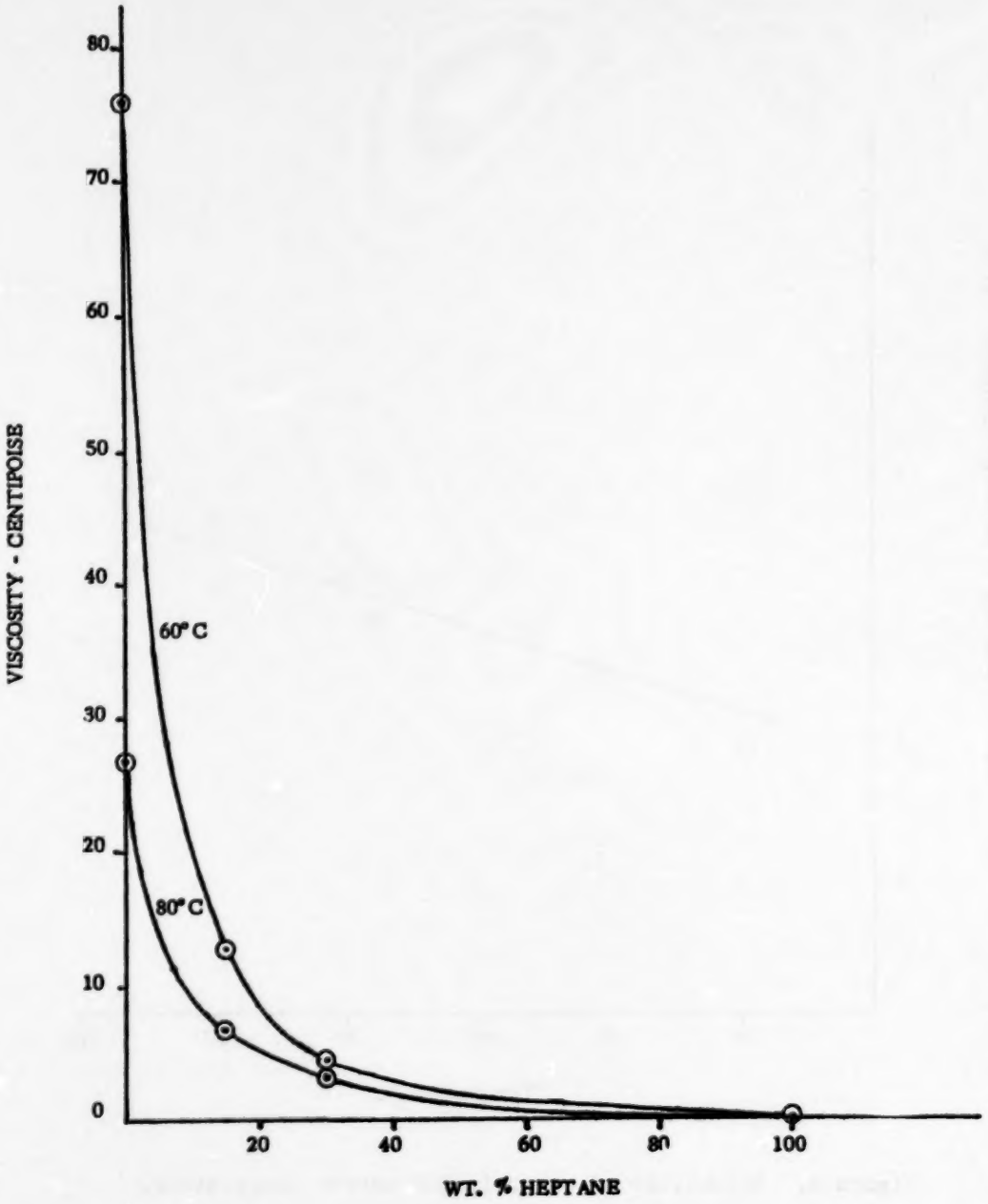

Figure 7. Viscosities of DDP-heptane mixtures.

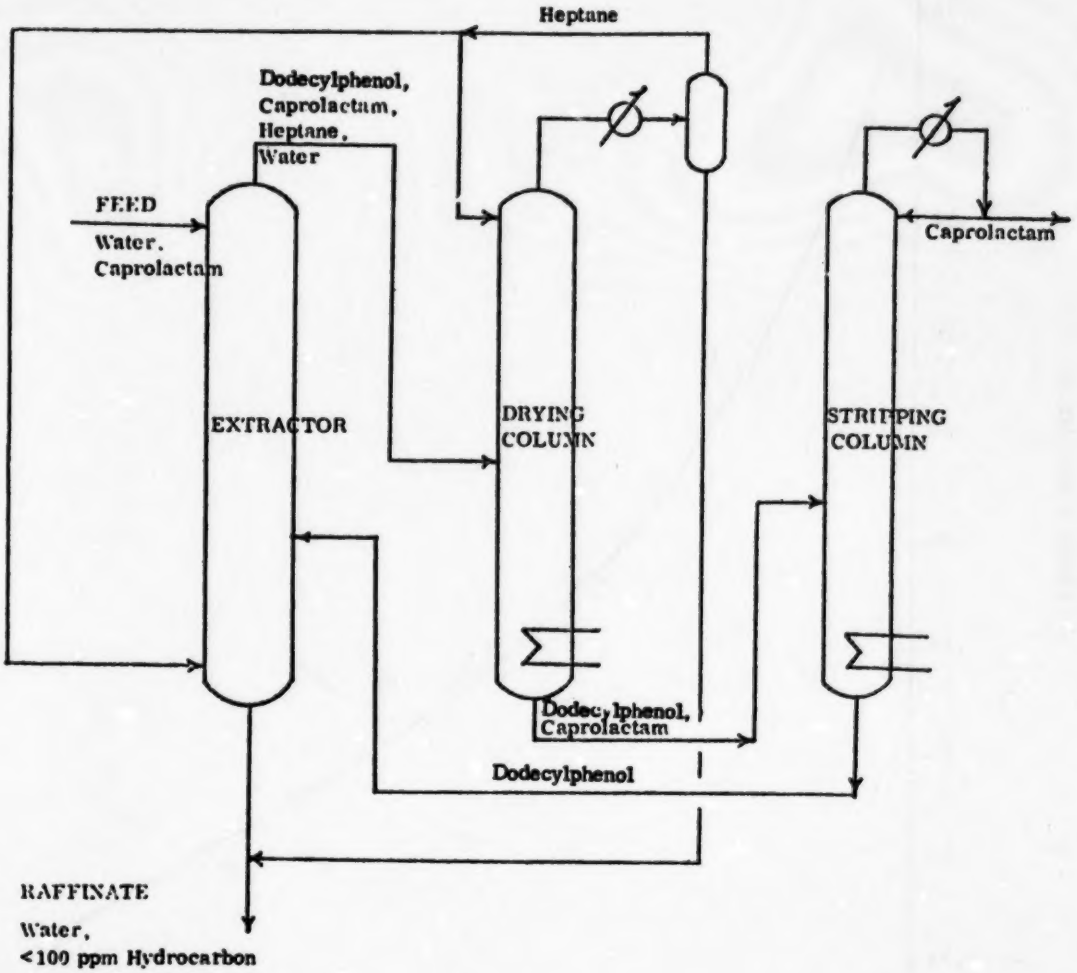

Figure 8. Modified Union Carbide Corporation process for caprolactam recovery from aqueous solution.

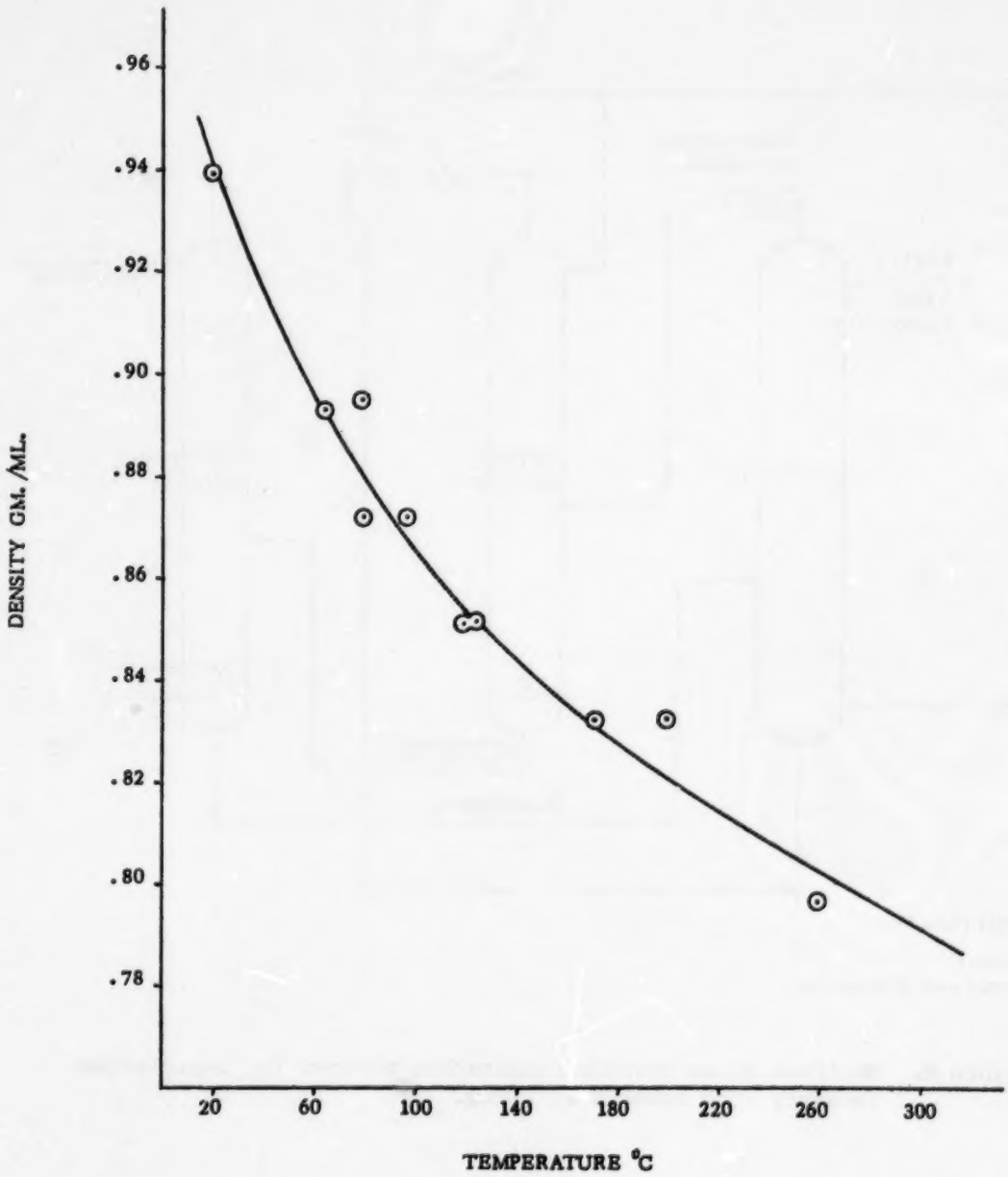

Figure 9. DDP density versus temperature.

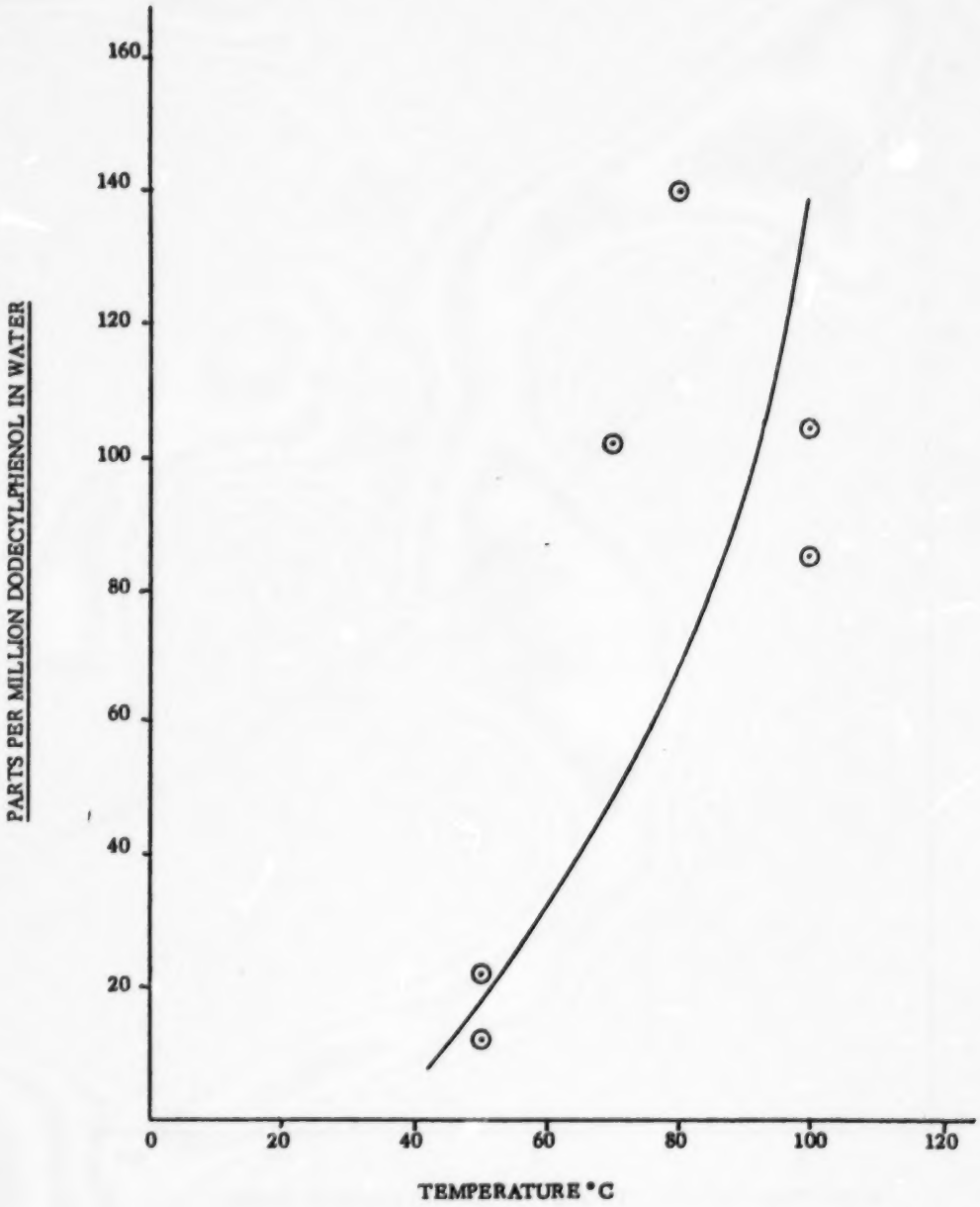

Figure 10. Solubility of DDP in water versus temperature.

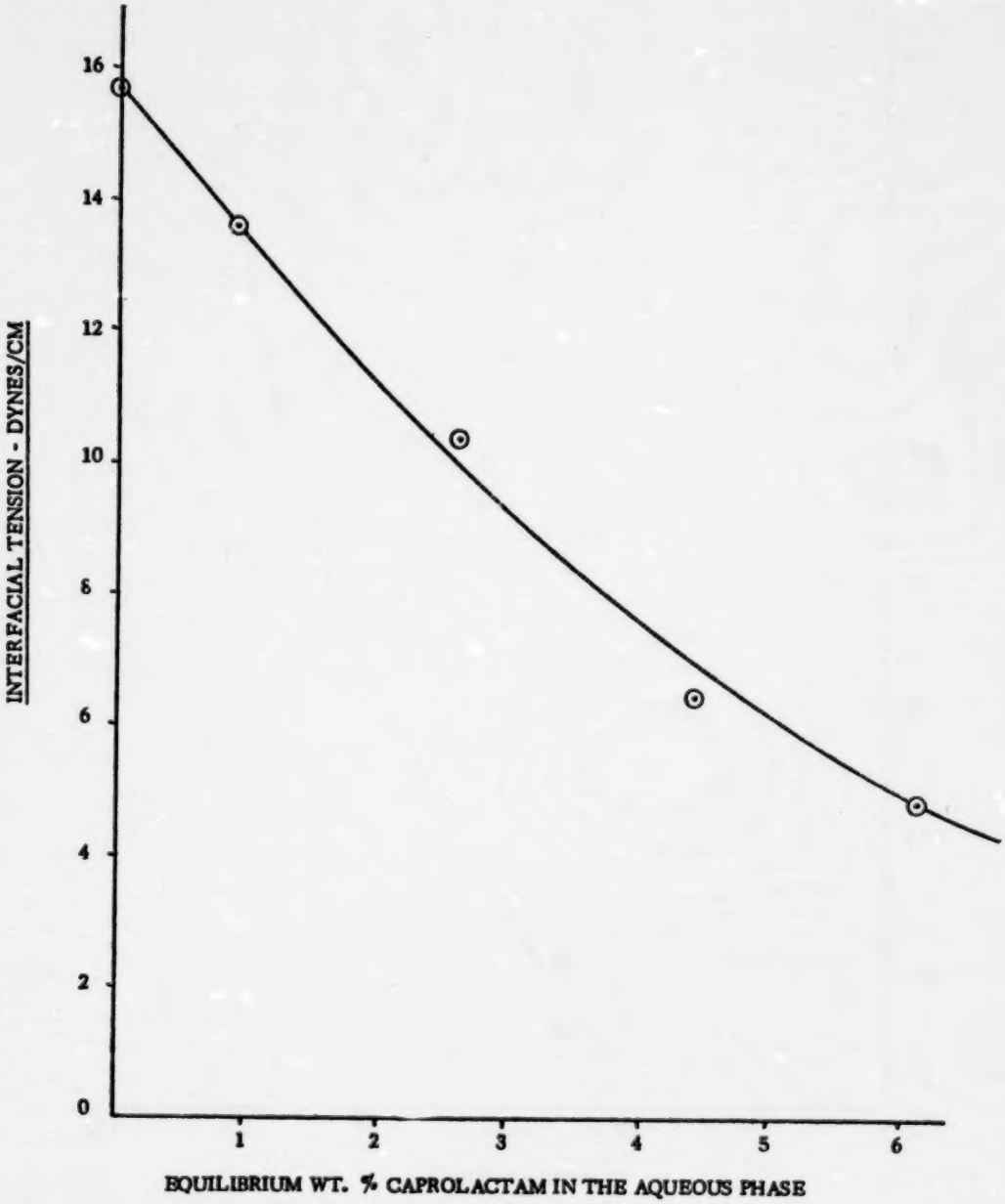

Figure 11. Interfacial tension of the water-caprolactam-DDP system at 80°C.

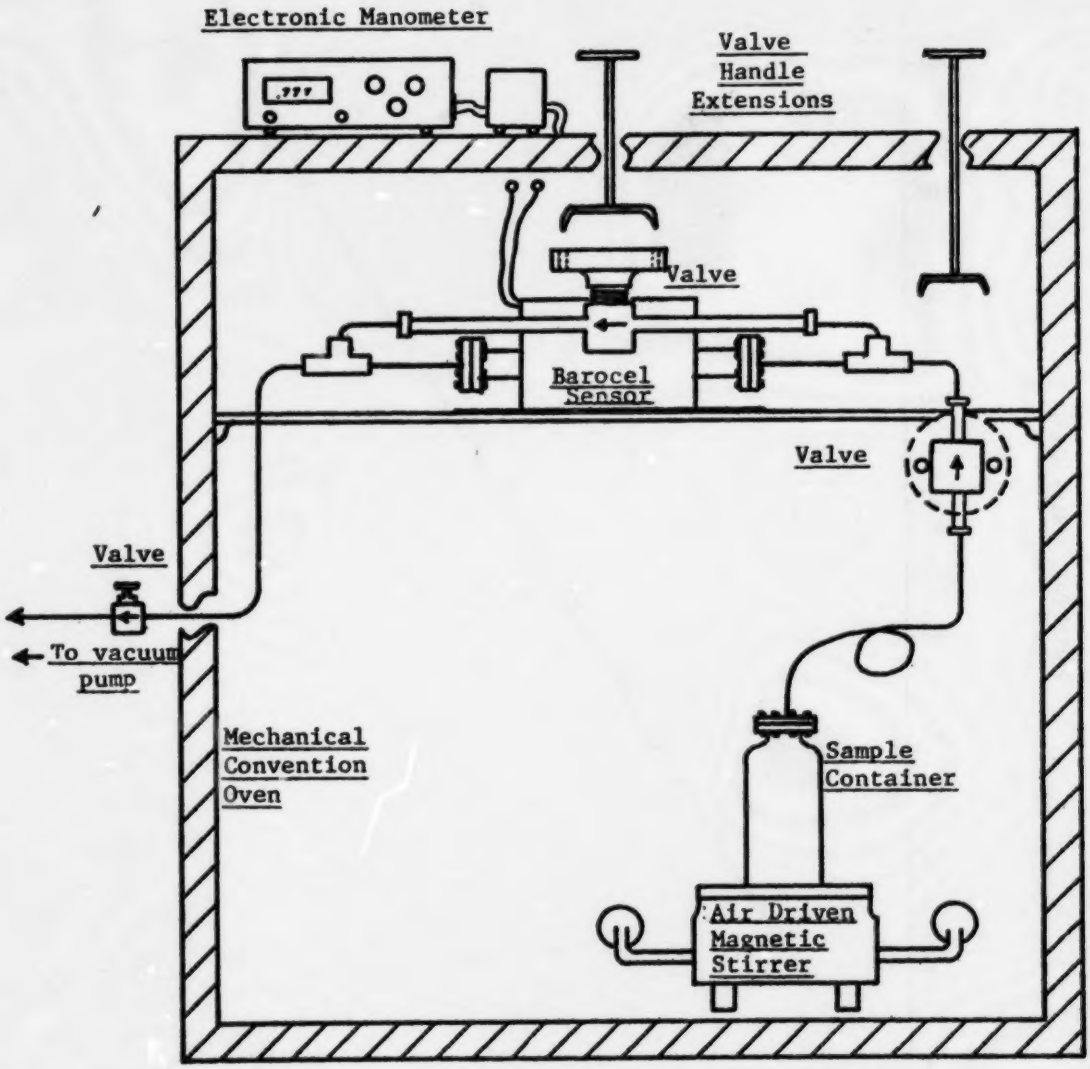

Figure 12. V.L.E. apparatus.

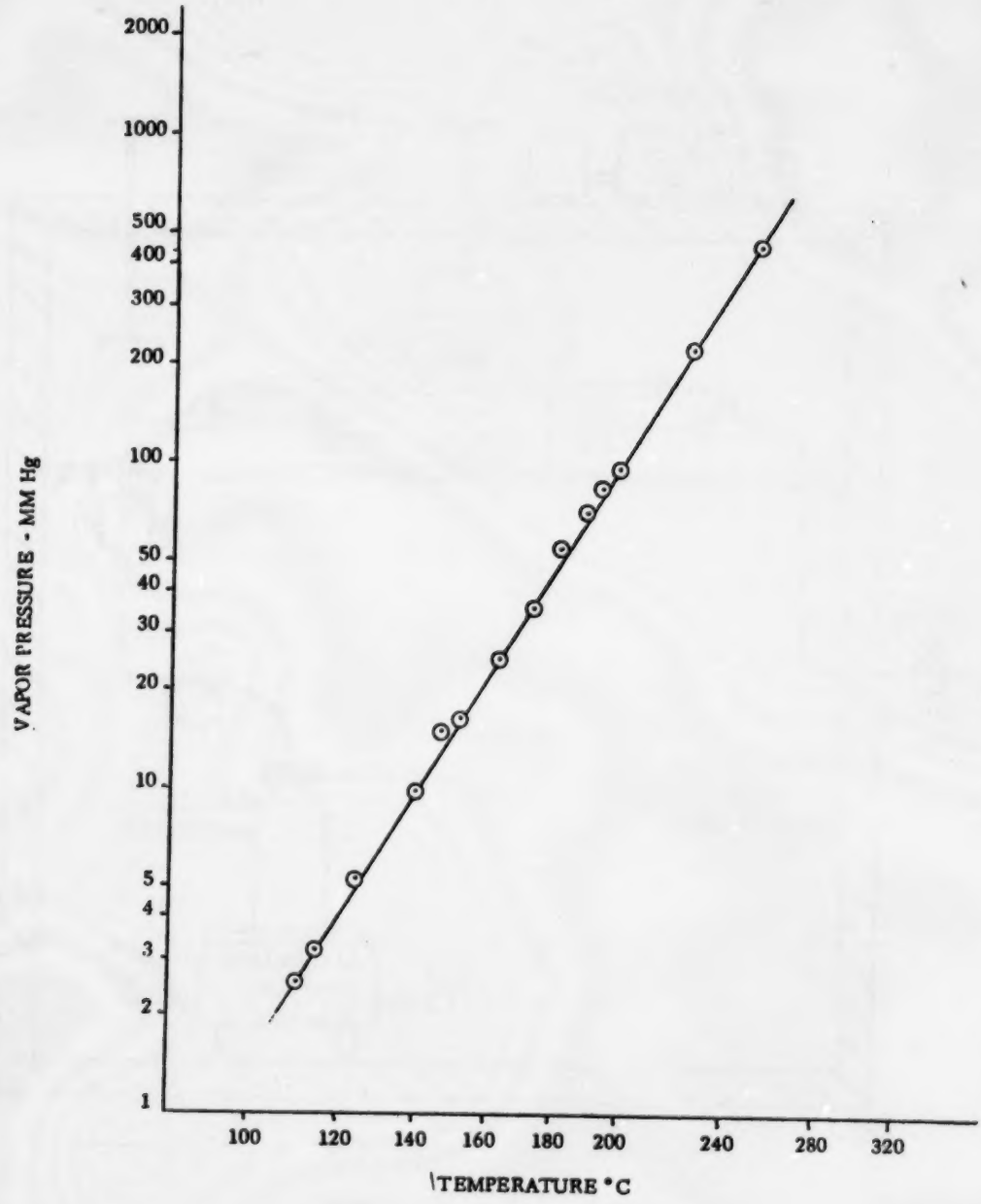

Figure 13. Caprolactam vapor pressure.

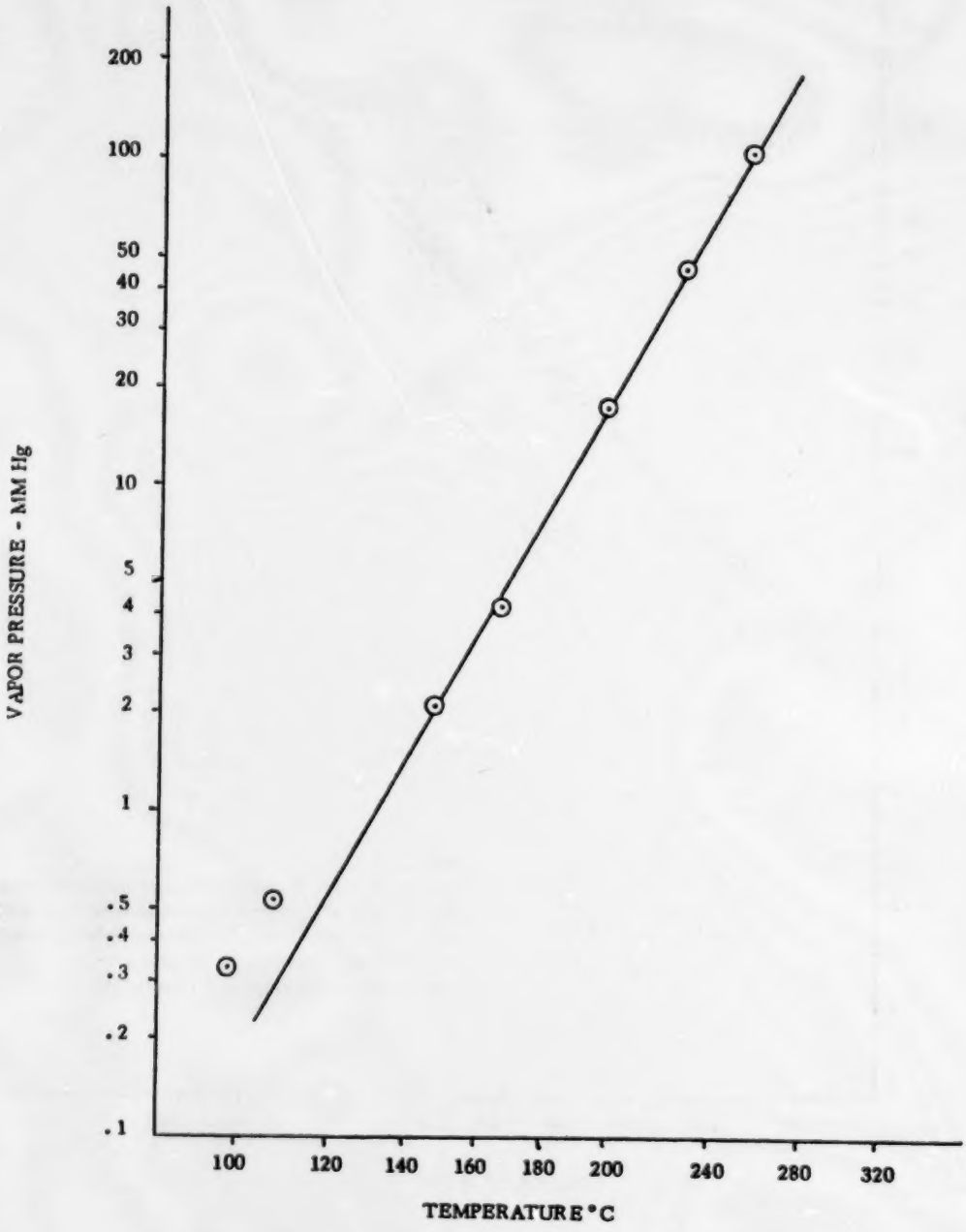

Figure 14. DDP vapor pressure.

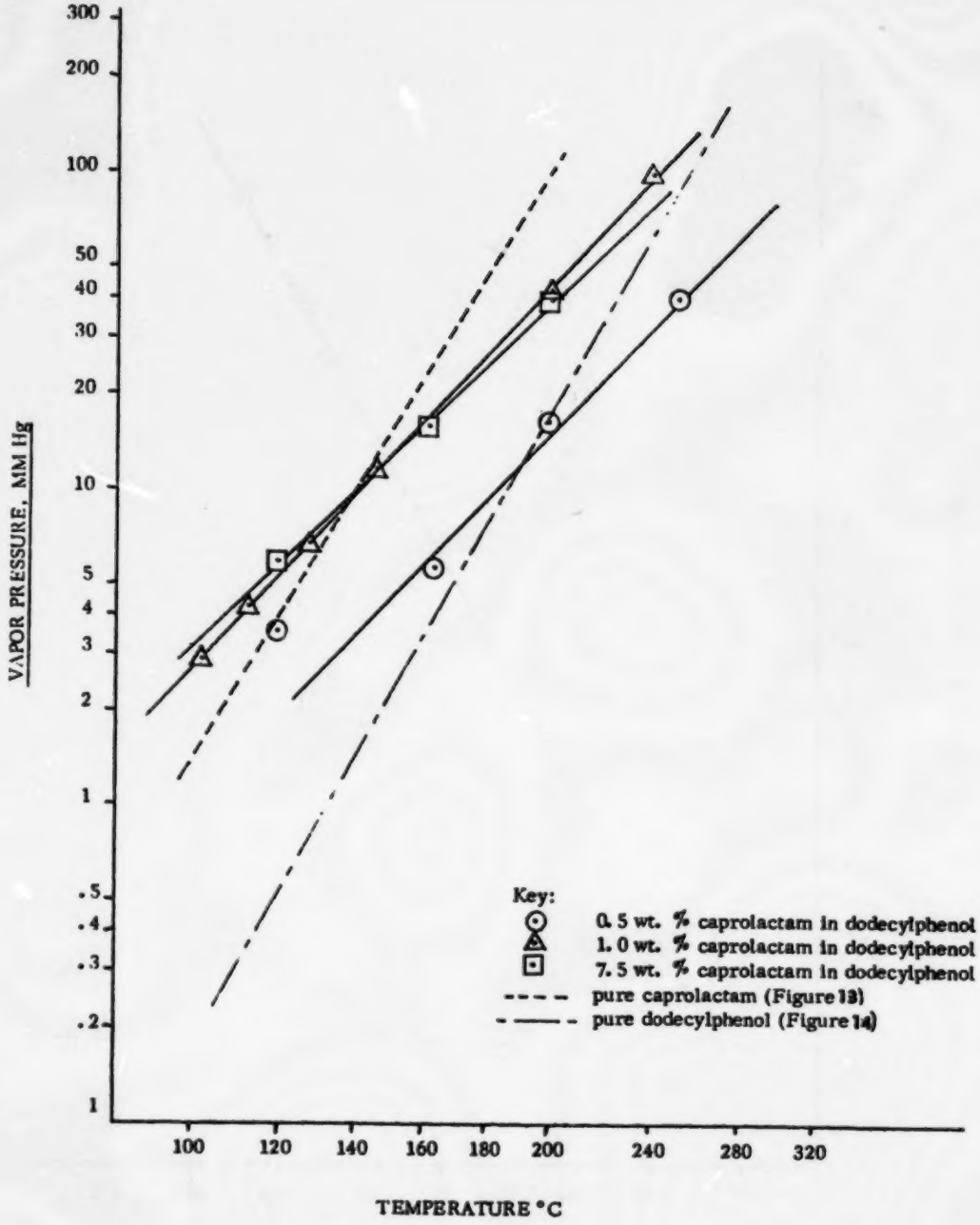

Figure 15. Vapor pressures of caprolactam-DDP mixtures.

TABLE 1. GAS CHROMATOGRAPH PARAMETERS FOR SAMPLES ANALYSIS

Sample Types	Raffinates, Feeds	Extracts, Lean Solvents
Column Material	Stainless Steel	Glass
Length	18 in.	6 ft.
Diameter	1/8 in. O. D.	2 mm I. D.
Liquid Phase	CARBOWAX 20M	-
Wt. %	5	-
Support	Gas Chrom Q	Tenax GC
Mesh	80/100	60/80
Carrier Gas	Helium	Helium
Inlet Press psig	91	91
Rate, ml./min.	20	20
Sample size, µl	0.8	0.8
Detector	Flame Ionization	Flame Ionization
Sensitivity	X 10	X 100
Hydrogen Press psig	18	18
Air Press psig	50	50
Detector Temp. °C	300	350
Inlet Temp. °C	250	300
Column Initial Temp. °C	170	150
Column Final Temp. °C	170	320
Rate	-	8% min.
Solvent	Isopropanol	Isopropanol
Internal Standard	Acetophenone	Acetophenone

TABLE 2. LABORATORY DISTILLATION OPERATING PARAMETERS

Column	Oldershaw, glass
Sieve plate spacing	2"
Number of plates	30
Column diameter	2"
Column head pressure	45 MM Hg
Final bottoms temperature	243°C
Caprolactam content of the bottoms product	592 ppm
Caprolactam content from similar distillation using pure caprolactam, dodecylphenol & water	520 ppm

TABLE 3. PILOT PLANT OPERATING PARAMETERS

Primary Extractor	
Column Type	Karr Reciprocating Plate
Shell Material	Glass
Plate Material	Teflon
Column Diameter	2 Inches
Plate Spacing	2 Inches
Number of Plates	45
Agitation Amplitude	.75 Inch
Secondary Extractor	
Column Type	Karr Reciprocating Plate
Shell Material	Glass
Plate Material	Teflon
Column Diameter	2 Inches
Plate Spacing	1 Inch
Number of Plates	63
Agitation Amplitude	.5 Inch
Distillation Column	
Column Type	Q.V.F.
Shell Material	Glass
Packing	1/4 Inch extruded protruded stainless steel
Packing Height	15 Feet
Column Diameter	4 Inches

TABLE 4. SUMMARY OF PILOT PLANT EFFICIENCY PROBLEMS

Problems	Suspected Cause	Action Taken	Results
Extractor efficiency H.E.T.S. - 35 in.	Poor lean solvent purity 1000-3000 ppm	Additional stripping, semi-continuous	No change
		Increase feed conc. 600-5280 ppm	No change
	Solvent viscosity	Change dispersed phase	No change
		Increase temperature	No change
		Add 30% heptane	98-99% recovery H.E.T.S.-16 in.
Lean solvent purity	Light ends	———	———
	Insufficient staging	Batch distillation	LS-466 ppm
Secondary extractor efficiency	Oversized column-insufficient interfacial contact	Change dispersed phase	No recovery-column wetting, higher viscosity of the dispersed phase
Solvent "decomposition"	Air leakage into column	Decomposition tests	Oxidative decomposition
		Laboratory extraction with "decomposed" solvent	Extraction performance unaffected

TABLE 5. PILOT PLANT DATA FOR CAPROLACTAM RECOVERY

Run Number	1A	1B	1C	1D	2A	2B	2C	2D	2E	2F
Primary Extractor										
Lean Solvent Flowrate ml./min.	15.2	20.0	20.0	20.0	20.0	20.0	20.0	32.0	32.0	32.0
PPM Caprolactam in Lean Solvent	1320	2489	1644	1406	968	1970	1689	2178	-	1917
Feed Flowrate ml./min.	161	161	161	161	161	161	161	161	161	161
PPM Caprolactam in Feed	600	600	600	600	600	600	100	1.04%	1.04%	1.04%
Dispersed Phase	DDP	DDP	DDP	DDP	DDP	DDP	DDP	DDP	DDP	DDP
Column Temperature °C	80	80	80	80	80	80	80	80	80	80
Agitation Speed, strokes/min.	340	340	340	340	340	340	340	340	450	250
Agitation Amplitude, in.	.4	.4	.4	.4	.4	.4	.4	.4	.4	.4
PPM Caprolactam in Raffinate	87.5	109.5	68	655	115	138	64	693	808	972
PPM DDP in Raffinate	1067	1510	124	94	1457	5145	2535	1.04%	1.58%	2137
Wt. % Water in Extract		-	-	-	-	-	-	-	-	-
Wt. % Caprolactam in Extract	0.523	.590	.530	.643	.525	-	1600	3.34%	-	-
% Caprolactam Recovery	85	82	89	-	81	77	36	93	92	91
Secondary Extractor										
Heptane Flowrate, ml./min.	5.0	7.0	9.0	9.0	7.0	7.0	7.0	7.0	7.0	7.0
Dispersed Phase	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane
Column Temperature °C	50	50	50	50	50	50	50	50	50	50
Agitation Speed, strokes/min.	530	530	530	530	530	530	530	530	530	530
Agitation Amplitude, in.	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5
PPM Caprolactam in Raffinate	57.8	118.2	242.5	176.8	48	98.8	102	713	-	923
PPM DDP in Raffinate	21.2	1550	30	< 9.2	305	275	39	538	-	325
PPM Heptane in Raffinate	-	-	-	-	-	-	-	-	-	-
PPM DDP in Extract	-	3630	2500	2650	High	High	-	-	-	-
PPM Caprolactam in Extract	-	67	518	549	270	63.7	-	-	-	-
Distillation Column										
Head Temperature °C	35	34	41.5	42	45	44.7	51.5	51.1	51.5	51.4
Feed Point Temperature °C	50	205	220	218	206	106	52.5	178	188.5	171.1
Bottom Temperature °C	243	238	243	246.7	241	250	> 250	> 250	> 250	> 250
Head Pressure, MM Hg	40	38	49	61.5	38.5	81.5	100	100	100	100
Reflux Ratio (reflux/total overhead)	.95	.60	.57	.58	.75	.70	.65	.40	.40	.40
Overhead	Water and Caprolactam									

(Continued)

TABLE 5 (continued)

Run Number	4H	4I	4J	4K	4L	4M	5A	5B	5C	5D
Primary Extractor										
Lean Solvent Flowrate ml. /min.	Primary and secondary extractors not operated during Runs 4-G--4-M						57	57	57	57
PPM Caprolactam in Lean Solvent						466	326	326	326	326
Feed Flowrate ml. /min.							164.6	164.6	164.6	164.6
PPM Caprolactam in Feed							.493%	.493%	.493%	.493%
Dispersed Phase							DDP	DDP	DDP	DDP
Column Temperature °C							60	60	60	60
Agitation Speed, strokes/min.							345	345	385	420
Agitation Amplitude, in.							.4	.4	.4	.4
PPM Caprolactam in Raffinate							44	-	29	28
PPM DDP in Raffinate							98	-	70	77
Wt. % Water in Extract							2.35	-	5.17	11.07
Wt. % Caprolactam in Extract							1.76	-	1.65	1.46
% Caprolactam Recovery							99	-	99.4	99.4
Secondary Extractor										
Heptane Flowrate, ml. /min.							5.3	5.3	5.3	5.3
Dispersed Phase							Aqueous	Aqueous	Aqueous	Aqueous
Column Temperature °C							50	50	55	55
Agitation Speed, strokes/min.							500	570	570	570
Agitation Amplitude, in.							.5	.5	.5	.5
PPM Caprolactam in Raffinate							32	-	22	23
PPM DDP in Raffinate							90	-	95	122
PPM Heptane in Raffinate							13	-	19	13
PPM DDP in Extract										
PPM Caprolactam in Extract										
Distillation Column										
Head Temperature °C	30	28	45.5	183	187	235	Distillation column not operated during Runs 5 A--5 D			
Feed Point Temperature °C	31	30	188	190	190	237.5				
Bottom Temperature °C	238	7520	249	249.5	249.5	>250				
Head Pressure, MM Hg	100	100	75	75	75	75				
Reflux Ratio (reflux/total overhead)	.30	.30	.20	.50	.10	.35				
Overhead	Heptane & Water	Heptane & Water	Heptane & Water	Light Ends	Caprolac-tam	DDP				

(Continued)

TABLE 5 (continued)

Run Number	2G	3A	4A	4B	4C	4D	4E	4F	4G
Primary Extractor									
Lean Solvent Flowrate ml./min.	32.0	35.0	55	55	55	55	55	55	-
PPM Caprolactam in Lean Solvent	-	3952	716	716	716	716	716	716	-
Feed Flowrate ml./min.	161	161	161	161	161	161	161	161	-
PPM Caprolactam in Feed	1.04%	.528%	.437%	.437%	.437%	.437%	.437%	.437%	-
Dispersed Phase	Aqueous	DDP	DDP	DDP	DDP	DDP	DDP	DDP	-
Column Temperature °C	80	92	80	80	80	60	60	60	-
Agitation Speed, strokes/min.	340	-	345	385	420	385	420	345	-
Agitation Amplitude, in.	.4	.4	.4	.4	.4	.4	.4	.4	-
PPM Caprolactam in Raffinate	951	549	102	304	63	120	66	179	-
PPM DDP in Raffinate	5662	3231	200	.211%	.292%	68	360	165	-
Wt. % Water in Extract	-	-	7.77	4.53	6.70	9.27	5.72	4.88	-
Wt. % Caprolactam in Extract	3.2	-	1.53	1.33	1.30	-	-	-	-
% Caprolactam Recovery	91	90	98	93	99	97	98	96	-
Secondary Extractor									
Heptane Flowrate, ml./min.	7.0	7.5	7.0	7.0	7.0	7.0	7.0	7.0	-
Dispersed Phase	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	-
Column Temperature °C	50	50	50	50	50	50	50	50	-
Agitation Speed, strokes/min.	530	530	500	500	500	555	555	555	-
Agitation Amplitude, in.	.5	.5	.5	.5	.5	.5	.5	.5	-
PPM Caprolactam in Raffinate	861	492	-	142	285	201	282	-	-
PPM DDP in Raffinate	288	1213	-	84	73	60	192	-	-
PPM Heptane in Raffinate	-	-	-	-	-	-	-	-	-
PPM DDP in Extract	-	-	-	-	-	-	-	-	-
PPM Caprolactam in Extract	-	-	-	-	-	-	-	-	-
Distillation Column									
Head Temperature C	-	54	Distillation column not operated during Runs 4-A--4-F						33
Feed Point Temperature °C	152	153							35
Bottom Temperature °C	>250	>250							70
Head Pressure, MM Hg	100	115							130
Reflux Ratio (reflux/total overhead)	.40	.75							.50
Overhead	Water and Caprolactam								Heptane and water

TABLE 6. BATCH CARBON ADSORPTION OF DDP AND CAPROLACTAM AT 80°C

Experiment No.	Carbon Type*	Solution/Carbon (wt./wt.)	PPM DDP in aqueous phase at equilibrium	PPM caprolactam in aqueous phase at equilibrium	K_d DDP (wt. % DDP in carbon) / (wt. % DDP in aqueous phase)	K_d caprolactam (wt. % cap. in carbon) / (wt. % " in aqueous phase)
Starting solution	-	-	38	103	-	-
1	Columbia LCL	10/1	N.D.** <9 ppm	N.D. < 2 ppm	> 32	> 505
2	"	50/1	"	"	> 161	> 2525
3	"	100/1	"	2 ppm	> 322	5050
4	Calgon CAL	10/1	"	N.D. < 2 ppm	> 32	> 505
5	"	50/1	"	"	> 161	> 2525
6	"	100/1	"	3 ppm	> 322	3333

* mesh - 375

** not detected

TABLE 7. CONTINUOUS COLUMN CARBON ADSORPTION OF PILOT PLANT SECONDARY EXTRACTOR EFFLUENT FROM RUN 5-C at 80°C

Carbon Used:	Columbia LCL, 12/28 mesh, 25 gms.
Column Glass:	1 1/2" I. D.
Carbon Bed Height:	10"
Flowrate:	.5 bed volumes/hr. (35 ml. /hr.)
Residence Time:	1 hour

Sample Analysis

Sample No.	PPM DDP	Caprolactam	Heptane	Total ml. of solution passed through bed
Starting Solution	95	25	19	-
1	N. D. <9	N. D. < 2	N. D. <10	130
2	"	"	"	210

TABLE 8. THERMAL STABILITY TESTS OF STRIPPED DDP

Oxidation Test	
Vessel	300 mls.
Sample size	20 mls.
Air purged, air atmosphere	10 Lbs. pressure
Duration of test	168 Hours
Color of starting material	Cloudy, yellow hue
Color after test	Dark Brown
Starting/residual pressure	10 Lbs./10 Lbs. at 20°C
Control Test	
Vessel size	300 mls.
Sample size	50 mls.
Nitrogen purged, nitrogen atmosphere	10 Lbs. pressure
Duration of test	168 Hours
Color of starting material	Cloudy, yellow hue
Color after test	Clear, slight yellow hue
Starting/residual pressure	11 Lbs./10 Lbs. at 20°C

TABLE 9. V.L.E. APPARATUS EQUIPMENT

Oven:	"Blue M" Horizontal air-flow Mechanical convection oven Model No. POM 206B-1 with a double glass observation panel built into the center of the oven door. Temperature range ambient to +343° C.
Pressure Transducer:	Datametrics Barocel Pressure Sensor Model No. 531D-100P-1B1-H7 Range - 0 to 100 psi differential, Accuracy to ± 0.03% of reading, Temperature capability to 450° C.
Pressure Readout:	Datametrics Electronic Manometer, Model No. 1174-A1A-1A1-A7 Display - 3 1/2 digit (digital readout) Accuracy - ± 0.05% of reading Readings are possible to as low as 1×10^{-4} psia.
Vacuum Pump:	Welch Duo-Seal two-stage pump, Free air capacity, 25 liter/min. at 580 rpm, Guaranteed pressure 1×10^{-4} torr. Hg. Pump series 1405, 1/3 hp motor.
Valves:	Nupro Bellow Valves SS-4H-TSW
Tube Couplings:	Cajon® VCR Vacuum Couplings
Flanges:	Varian Associates Mini-conflat flanges using OFHC copper gaskets.

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APPENDIX

EXPERIMENTAL METHODS USED IN OBTAINING PHYSICAL PROPERTY DATA

PHYSICAL PROPERTY MEASURED	METHOD USED	COMMENTS
Density	Pycnometer in a constant temperature bath	Can be calibrated with water at temperatures below 100°C and with ethylene glycol at temperatures above 100°C
Solubility of dodecylphenol in water Solubility of water in dodecylphenol	Extraction apparatus (Figure 1)	Entrainment can cause large error especially below 100 ppm. Minimizing system stirring helps to prevent entrainment. This problem could be eliminated by filtering the phases (at the system temperature, of course), however the apparatus would be more complex.
Interfacial tension of the water-caprolactam-dodecylphenol system	Tensomat ring tensometer	With skill and patience, will give good results at temperatures below the mixture boiling point.
Dodecylphenol viscosity Heptane-dodecylphenol viscosity	Cannon-Fenske capillary viscometer	Standard, very satisfactory equipment

GLOSSARY

extract: Solvent (dodecylphenol)* that has been used in an extraction and contains the desired extractable component (caprolactam). Generally, a small fraction of the second phase (water) is dissolved in the extract.

lean solvent: Solvent which has been regenerated from its extract mixture by distillation or other means.

raffinate: The liquid phase (water) which has been depleted of one or more components (caprolactam) by an extraction.

solvent: A liquid phase (dodecylphenol) which is used to extract a desired component (caprolactam)from a second immiscible phase (water).

* compounds in parentheses apply to the process in this report